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13. ABSTRACT *(Maximum 200 Words)*

The objective of the project was to develop new polymeric materials for second-order nonlinear optical (NLO) applications, specifically electro-optic applications. Alkoxysiloxane derivatives of organic azo dye chromophores were synthesized and used to prepare NLO siloxanes by the sol-gel reaction with a siloxane polymer. The dipole moments and polarizabilities and hyperpolarizabilities of the chromophores were calculated by semi-empirical quantum mechanical modeling.

A novel approach using interpenetrating polymer networks (IPN) combining a sol-gel based NLO siloxane with a thermally crosslinkable NLO azo dye attached epoxy network, as stable second-order NLO materials was also introduced. In two of these systems, the addition of another crosslinkable azo dye component to boost the NLO density was investigated. The materials were processed into thin films on substrates and simultaneously oriented by corona poling and thermally cured at temperatures up to 220 °C.

The NLO siloxanes showed relatively weak optical nonlinearities while the electro-optic coefficients of the IPN systems were reasonably large and the temporal stability was excellent - the materials showing considerable promise for practical applications. The design, synthesis, and fabrication of the polymers and the characterization of their linear and nonlinear optical properties, thermal stability, and optical loss, were described.

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for
Optical Switching and Modulation

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I. Introduction

This is the final technical report from Molecular Technologies Inc. (MTI) on "Organosilicon Polymeric Nonlinear Optical Materials for Optical Switching and Modulation," contract number F49620-93-C-0039. The work has been performed by Dr. Mario Cazeca, Dr. Jeng-I Chen, Dr. Lian Li, Dr. Sutiyao Marturunkakul and Mr. Sandip Sengupta of MTI. Part of the work was carried out under a subcontract by the University of Massachusetts Lowell. Consultation has been provided by Dr. Jayant Kumar of the same university. This report was prepared by the principal investigator, Mr. Sandip Sengupta (tel. no. 508-392-1304), and Ms. Dianne Galotti (tel. no. 508-458-8915) of MTI.

IIa. Project Summary

The Phase I work was initiated with the primary objective of developing second-order nonlinear optical (NLO) organic polymers for electro-optic (EO) device applications. High temporal stability of the optical nonlinearity, coupled with an EO coefficient r, as large as possible, was the main design goal. The initially proposed material system was **NLO siloxane** polymers prepared from the alkoxysilane derivatives of organic NLO chromophores such as azo dyes. Subsequently the work was extended to include multicomponent **IPN systems** with NLO siloxane polymers as a major constituent, because of the excellent temporal stability offered by these systems.

As in all second-order NLO polymers, the NLO properties were activated by orienting the molecular dipoles in a high external electric field, generated in this case by the well established technique of corona poling. Molecular modeling of chromophores and optical characterization of thin film samples were carried out in support of the development of the polymeric materials by organic synthetic techniques.

All of the research objectives were **met or exceeded**. In particular, the number of different polymer systems studied, **substantially** exceeded the scope of the original proposal. With the help of the SBIR funding provided by the AFOSR in Phase I, several new NLO

polymers with **high temporal stability** and reasonable r values (to 6.5 pm/V at 1.3 μm) were prepared. The Phase II work will seek to build upon these developments, to produce polymers with even better temporal stability, higher r coefficients and lower optical loss.

IIb. Statement of Work (SOW)

The SOW, from the contracting document is shown :

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1. Chromophores with optimized hyperpolarizability and absorption characteristics will be selected for further study.

2. Precursors will be synthesized from the selected chromophores by coupling alkoxysilane groups as attachments.

3. Optical quality thin films will be fabricated by spin coating and second order nonlinearity will be induced by corona poling.

4. The NLO and linear optical properties of these films will be characterized.

5. The temporal stability of these films will be determined.

As mentioned earlier, all of these tasks were satisfactorily completed for a number of different chemical systems and extremely encouraging results were obtained.

III. Technical Section

We now discuss the technical details of the project. The overall development of the NLO polymers is discussed first, including the **theoretical modeling** of the chromophores, followed by their **optical properties**. Details of the fabrication of samples, organic syntheses, and procedures for the **optical characterization** of the samples are covered in the appendices.

Materials Development

The development of the NLO polymers is described in essentially chronological order. We first describe all siloxane systems followed by multicomponent interpenetrating network (IPN) systems incorporating NLO-active siloxane polymers. A number of these polymer

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systems were synthesized and thoroughly characterized in terms of their chemical behavior and their linear and nonlinear optical properties.

IIIa. NLO Siloxanes

Earlier work in our consultant's laboratories by Jeng et. al [1] has shown that azo dyes can be covalently attached to a siloxane matrix via the sol gel condensation of their alkoxysilane derivatives. The rationale for using the alkoxysilane dyes (ASDs) is as follows:

1. Facile incorporation of the core chromophore into the siloxane network.

2. Larger chromophore size (to reduce loss of the chromophore during thermal

   processing).

In the present work, the azo dyes, chromophore 2 [4(4'-nitrophenylazo)-1-naphthol] and chromophore 3 [4(4'-nitrophenylazo)resorcinol], were chosen as the core chromophores, and the corresponding alkoxysilane derivatives, ASD2 and ASD3 were synthesized.

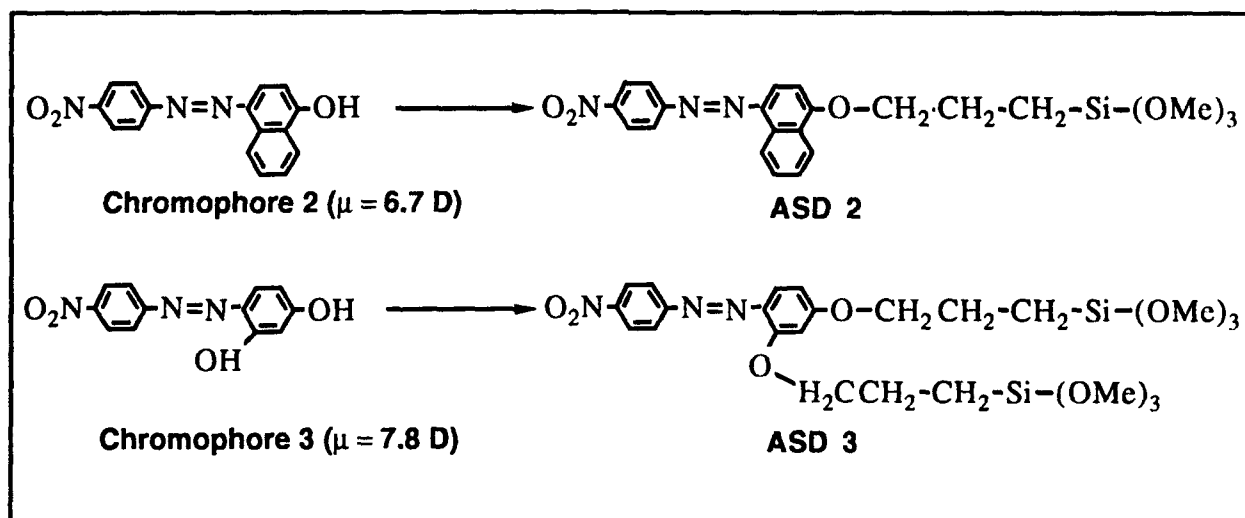

Figure 1. Structures of the chromophores and the corresponding alkoxysilane dyes.

The chosen chromophores were expected to have somewhat higher $\mu\beta$ (dipole moment x second-order hyperpolarizability) values than the structurally similar azo dye [4(4'-nitrophenylazo)aniline] (Disperse Orange 3, DO3), used in [1]. In addition, ASD3, with two alkoxysilane moieties, was expected to provide a more highly crosslinked and hence more

stable molecular architecture. Accuglass 204, a commercially available phenyl siloxane polymer in alcohol solvents, was used as the second component for the sol gel reaction, because of its excellent film forming qualities [2]. The formula provided by the manufacturer is shown [3]:
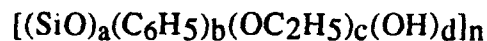
$$[(SiO)_a(C_6H_5)_b(OC_2H_5)_c(OH)_d]_n$$
$$\text{where } a \geq 1 \quad b,c,d \geq 0.5 \; ; n = 5\text{-}100.$$

Developed by Allied-Signal, Accuglass 204 is normally used in the semiconductor industry, as a spin-on-glass (SOG) material [4], to deposit a planarizing and isolating glass layer on silicon integrated circuits by spin coating. In this application, the spun-on material is subjected to a low temperature bake (100-200 °C), followed by a vitrifying high temperature bake at ~425 °C [3] in a nitrogen atmosphere, a temperature much higher than our process temperature for using it as a matrix for NLO chromophores.

When these ASDs were incorporated into Accuglass 204, and cured at 175 °C, however, most of the dye was lost by sublimation, before sufficient crosslinking could take place to lock the dye in place, inside the polymer matrix. To circumvent this problem, as we had originally proposed, rapid thermal processing at >200 °C was attempted to minimize dye loss during curing.

Chromophore 3 and its corresponding alkoxysilane derivative ASD3 were found to be less stable at higher processing temperatures. Hence further efforts were concentrated on chromophore 2 and its ASD2 derivative.

A solution of ASD2 and Accuglass 204 in mixed solvents, which contained about 10% of nonlinear optical (NLO) chromophores, was used for spin-coating thin films. Spin-coated samples on glass microscope slides were simultaneously corona poled and cured at 220 °C for 30 minutes. The NLO properties and their temporal stability of the resulting films were investigated by monitoring the second harmonic generation (SHG) with Nd:YAG radiation. Experimental details are given in Appendix B. Our studies indicate that these samples

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exhibit **good temporal stability**, with 90% of the optical nonlinearity retained after 83 hours at 25 °C, and 74% after the same interval at 110 °C. The absolute NLO coefficients, $d_{33}s$, were only of the order of 1 pm/V, indicating that most of the dye was still degraded or lost by sublimation.

Since the maximum processing temperature could not be increased much further without complete loss of the dye by sublimation, alternate techniques such as the incorporation of core chromophores in the form of an oligomer or polymer, to minimize dye loss during curing, were considered. This search for a better approach to NLO polymers based on sol-gel systems led us to further improvement of the previously mentioned **IPN** systems. The presence of a **second NLO polymer component** synergistically **stabilizes** both NLO polymer components against **relaxation** effects. IPN systems exhibit enhanced temporal stability by the formation of high glass transition temperature (T_g) and high crosslinking density matrices and **prevent** dye loss during the critical curing step, by lowering the required reaction temperature. The IPN systems also avoid the problems of phase separation that are often encountered when attempts are made to incorporate non-siloxane NLO polymers into a siloxane polymer system [5].

IIIa.1 Chromophore Design and Characterization

In our choice of suitable chromophores, we were guided by a combination of past experience, chemical intuition, molecular modeling, and related work by other investigators.

Chromophore Optimization

For large second-order nonlinearity, chromophores with large $\mu\beta$ are required [6]. In addition, for incorporation in a siloxane matrix, the core chromophore must incorporate functional groups such as hydroxyl moieties for facile attachment of alkoxysilane functions and be as thermally stable as possible to withstand the high temperature thermal processing required for matrix formation [1]. We chose suitable azo dyes for our initial studies, since they are relatively well understood, readily available and our investigators had previous experience in working with them. The dyes used, have their absorption peaks in the blue

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($\lambda_{max} < 500$ nm), and are essentially transparent in the 830 nm to 1.5 μm region, which is of most importance for applications in EO devices. Chromophores with even higher $\mu\beta$ values, such as tricyanovinyl derivatives will be utilized in the proposed follow on Phase II project.

Molecular Modeling

Molecular modeling of the core chromophores were carried out using MOPAC [7], with input data file generation by CHEMNOTES (Polygen, Waltham, Massachusetts), on an IBM RISC/6000 computer. These were semi-empirical computations utilizing a finite-field approach. Calculations were primarily carried out using the PM3 Hamiltonian, although the AM1 (Austin Model 1) Hamiltonian was also used. The dipole moments of the core chromophores chromophore 2 and chromophore 3 were determined by this method. The exchange contribution to the dipole moments have now been included and the resultant values are now in better agreement with both experimental and theoretical values for similar compounds, than the point-charge values reported in the first progress report [8]. The zero-frequency, first order polarizability, and second and third order hyperpolarizabilities, α, β and γ were also calculated. As a check on the computation, μ, α, β and γ were also calculated for structural analogs of the chromophores and for model compounds such as MNA (2-methyl-4-nitroaniline) and PNA (*p*-nitroaniline). Our results were found to be in essentially exact agreement with similar computational values in the literature [9].

Table 1. Molecular modeling results for chromophores.

Parameter	Chromophore 2	Chromophore 3	MNA	PNA
μ (Debye)	6.651	7.815	6.739	6.639 (6.64)
α (x 10^{-23} esu)	5.698	4.667	2.427	2.191
β (x 10^{-30} esu)	13.93	12.08	5.04	5.16 (5.27)
γ (x 10^{-36} esu)	77.96	57.07	10.54	10.10

Values within parentheses are PM3 results from Burland *et al.* [9]. We have followed their lead in multiplying the MOPAC β values by 5/6 to match the more common definitions of β and its vector component.

For semi-empirical calculations such as ours, we expect that the calculated β values are only approximate and most likely somewhat underestimated while the dipole moments are slightly overestimated. However, it is reasonable to assume that the relative trends in the molecular parameters, particularly between these structurally similar chromophores are accurately predicted [9].

Thin Film Sample Preparation and Characterization

Thin films of the electrooptical polymer compositions on glass substrates were cured and oriented in a corona poling apparatus provided with an aluminum hot stage, which could be heated electrically or cooled by circulating water through cooling passages in the stage. The poling apparatus is described in Appendix B.

A solution of ASD2 or ASD3 and Accuglass 204 in mixed solvents, which contained about 10% of nonlinear optical (NLO) chromophores, was used for spin-coating thin films. Initially the curing temperature was 170-175 °C, with a curing time of 4 hours. As mentioned earlier, the NLO chromophore was almost completely lost or degraded in this time interval. Therefore higher curing temperatures for a shorter interval were used.

In a typical procedure, ASD2 (0.077 g) was dissolved in 1-methyl-2-pyrrolidinone (4 ml), Accuglass 204 (10 ml) was added, and most of the alcohols (ethanol and propanol solvents from the Accuglass) were removed in a Büchi rotary evaporator. Dimethylbenzylamine (20 μl) was added as a base catalyst for the sol-gel reaction, and the resulting solution, which contained about 10% of nonlinear optical (NLO) chromophores, was used for spin-coating thin films. Samples were spin-coated onto glass microscope slides at a spin speed of 600 rpm, in a Headway Research spin coater. They were simultaneously corona poled and cured at 220 °C for 30 minutes. The NLO properties and temporal stability of these properties in the resulting films were investigated by monitoring the second harmonic generation with Nd:YAG radiation. As mentioned earlier, these samples exhibit good temporal stability, with 90 % of the d_{33} values retained after 83 hours at 25 °C, and 74 % after the same interval

at 110 °C, but the absolute d_{33} values were still of the order of 1 pm/V, indicating that most of the dye was still degraded or lost by sublimation. The optically clear films exhibited some microscopic cracks, which could probably be prevented by further process optimization, or the use of a more crack resistant Accuglass host such as the T-14 series of materials [3].

We now describe the work on the temporally stable nonlinear optical IPN systems.

IIIb. NLO Siloxane-NLO Epoxy IPN systems

In collaboration with the University of Massachusetts Lowell, we have been working on the novel IPN approach, which has given excellent results in terms of **improved d_{33} values** and **extraordinary temporal stability at elevated temperatures**. Instead of incorporating the chromophores in the form of an oligomer or polymer in an Accuglass matrix, in the IPNs developed during the Phase I research, the alkoxysilane dye is made to undergo a sol-gel reaction with a multihydroxyl phenoxyl molecule, forming a phenoxysilicon polymer network. An NLO epoxy network is simultaneously formed by the condensation of the corresponding prepolymer. The two polymer networks interpenetrate, forming a molecular level polymer blend, the **IPN** system [10,11]. Two types of epoxy networks have been developed based on an NLO linear epoxy polymer functionalized with thermally crosslinkable groups. The NLO density is further increased by the incorporation of additional crosslinkable NLO dyes into the epoxy network. The **temporal stability of the** IPNs are excellent, as discussed in the subsequent sections.

IPN-A System

We have continued work on an NLO-active IPN composite [11] originally developed by two of our investigators, Dr. Jeng I. Chen and Dr. Sutiyao Marturunkakul, during their tenure at the University of Massachusetts Lowell.

This system, henceforth referred to as the **IPN-A** system, consists of an NLO phenoxysilicon polymer network and an NLO epoxy-based polymer network, with interpenetrating network formation by simultaneous thermal polymerization of the precursors

to the two network components. The NLO-active epoxy network is formed by a free radical addition reaction of the prepolymer BPAZO containing crosslinkable acryloyl groups (Fig. 2).
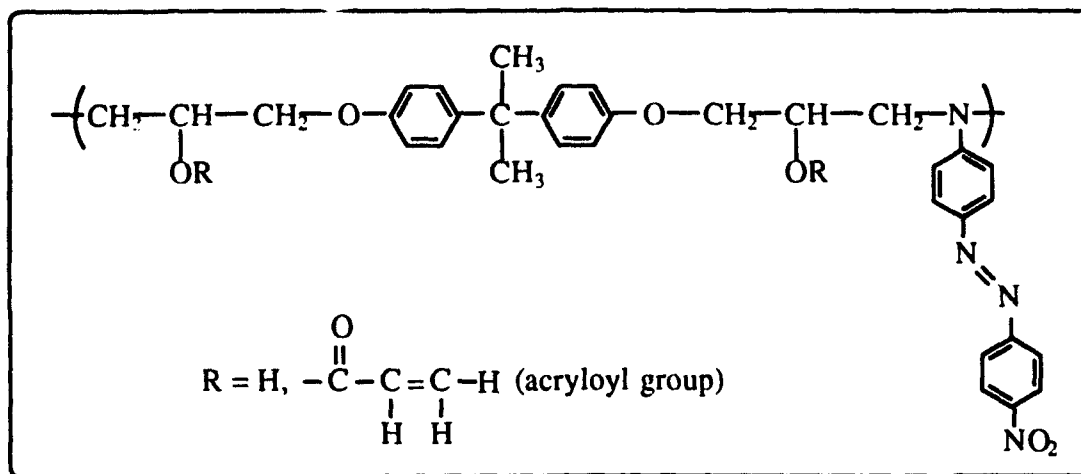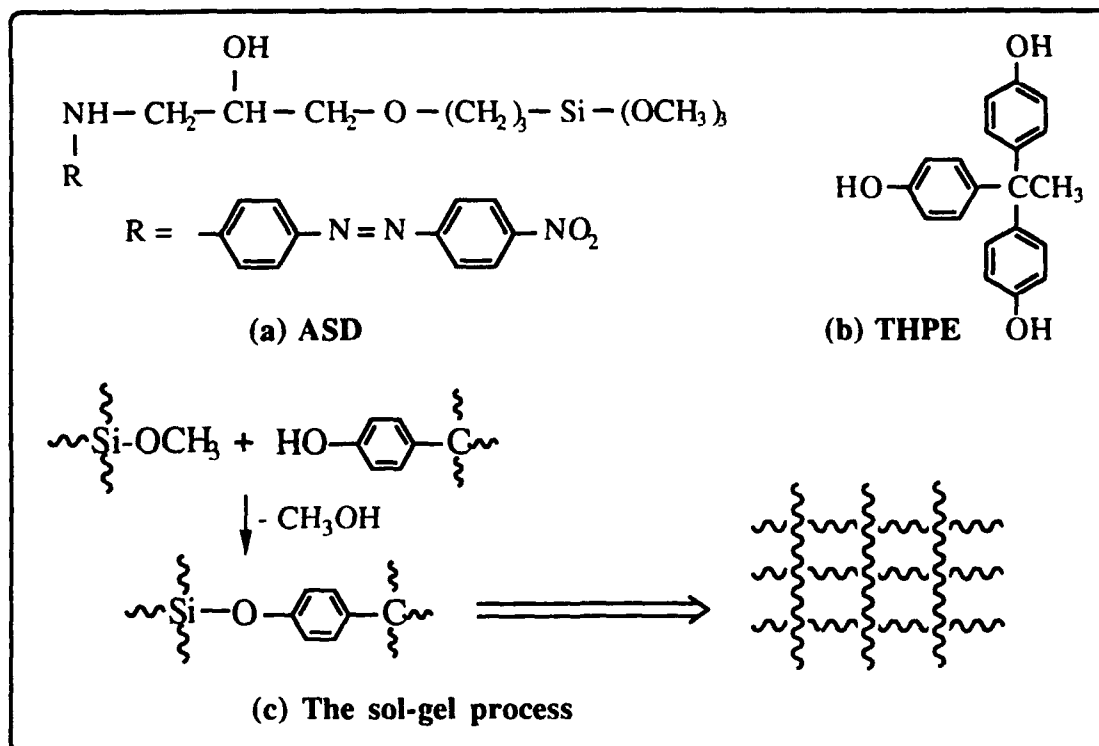

Figure 2.   The chemical structure of BPAZO.

Figure 3.   Chemical structures of (a) ASD and (b) THPE. The formation of the phenoxysilicon polymer network via a sol-gel process is shown in (c).

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The phenoxysilicon polymer (Fig. 3) is formed *via the sol-gel reaction* between 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) and the ASD of (3-glycidoxypropyl)trimethoxysilane and Disperse Orange 3 [the same azo dye chromophore attached to BPAZO]. The two polymer networks form simultaneously in a noninterfering manner, and no phase separation is observed [11].

Characterization of the IPN-A system:

1) The refractive indices of the spin coated, cured IPN samples were measured with a Rudolph Research ellipsometer at various wavelengths, and are listed below.

Table 2. Refractive Indices of IPN-A Polymer Films

Wavelength (nm)	Index of Refraction	Wavelength (nm)	Index of Refraction
532	1.778	775	1.655
633	1.694	830	1.650
671	1.683	1000	1.637

2) The second-order NLO properties of the poled IPN samples were measured by the SHG technique at the 1.064 μm and 1.542 μm (Raman shifted in methane) wavelengths from a Q-switched Nd:YAG laser. Again, the experimental details may be found in Appendix B. The relaxation behavior of the second-order NLO properties was studied by monitoring the decay of the second harmonic intensity with 1.064 μm laser radiation as a function of time at 110 °C. The IPN system shows **no measurable decay** of d_{33} coefficient after being heated at **110 °C** for over **1000 hours**, which is shown in the Fig. 4 below. The d_{33} values of the poled IPN sample were measured to be **33 pm/V** (same as in ref. 11) and 5.5 pm/V at 1.064 and 1.542 μm, respectively.
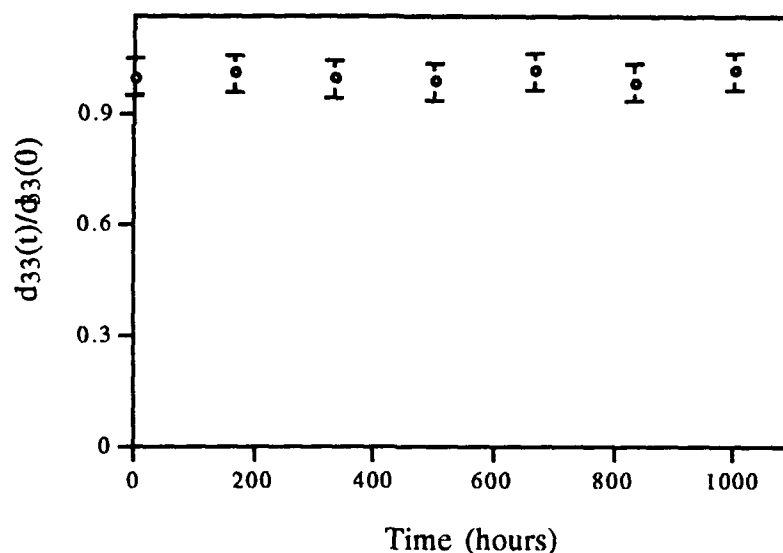
Figure 4. Temporal Stability of the IPN-A System.

3) Additionally, the **EO** coefficients of the IPN-A samples were measured at 633 nm and 1.3 μm, using the reflection method reported by Teng and Man[12]. Experimental details are given in the Appendix. *The measured r_{33} coefficients were ~ 17 pm/V at 633 nm and 5 pm/V at 1.3 μm.*

4) Optical loss measurements were made by waveguiding techniques on polymer slab waveguides. Again the procedure is described in detail in Appendix B. The optical loss is relatively high and thus difficult to measure.

Systems of this type, thus show considerable promise as practical nonlinear optical materials. Since the temporal stability was very encouraging, we vigorously pursued similar systems that promised higher r coefficients and lower optical loss.

Two **new** interpenetrating network (IPN) systems were **synthesized** and studied. These differ from the system reported earlier, in that the epoxy component was replaced by new NLO epoxy sytems with higher concentrations of NLO functionalities. They are thus **chemically distinct** systems, although the basic design philosophy has been retained and

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extended. The same phenoxysilicon polymer (ASD/THPE) [13], shown in Fig. 3, which was utilized in the IPN-A system [11] was used as the second IPN component.

IPN-AB System

The first system combines the network of NLO active phenoxysilicon polymer and the network of BPAZO, the epoxy of the diglycidyl ether of bisphenol A and Disperse Orange 3 with the addition of the thermally crosslinkable azo dye, 2,4 acryloyloxy (4'-phenylazonitro-benzene) (APAN). The chemical structure of BPAZO has been shown earlier; that of APAN is shown below. The BPAZO-APAN system has been studied earlier [14], but not as a component of IPN systems.
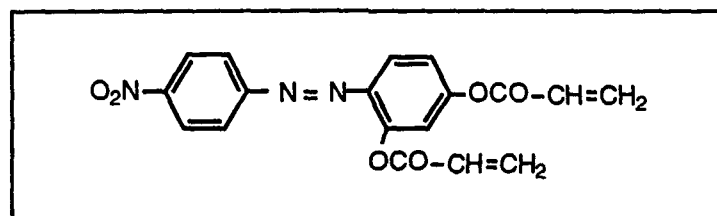

Figure 5. The chemical structure of **APAN**.

The dye APAN, is functionalized with acryloyl groups, which can react with the acryloyl groups of BPAZO to form a network. Thus the addition of APAN is expected to result in an increase in the NLO density (and consequently **higher** d and r coefficients) and in a higher crosslinking density (for improved temporal stability). IPNs of two compositions of ASD/THPE and BPAZO/APAN system were prepared and characterized, as summarized in Table 3. We refer to it as the IPN-AB system, since it may be considered an enhanced IPN-A system.

Table 3. IPN-AB (ASD/THPE and BPAZO/APAN) Samples Prepared and Studied.

	Phenoxysilicon (ASD/THPE)	BPAZO-APAN (2:1 w/w)	Processing Conditions	d_{33} at 1.064 μm
Weight	1	1	1h @ 200 °C	25.5
ratio	2	1	1h @ 200 °C	22.0

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IPN-B System

The second system utilized a newly synthesized bisphenol A based epoxy, namely **Polymer-11**. This polymer contains the same Disperse Orange 3 (DO3) NLO dye as BPAZO, but carries crosslinkable methacryloyl functionalities inserted via the corresponding acid chloride. The functionalization of methacryloyl can be essentially **100 per cent**, whereas in the case of acryloyl (as in BPAZO), usually only about 30 per cent functionalization can be achieved. Again, the higher level of functionalization leads to higher crosslinking densities, with its attendant advantages. Also, differential scanning calorimetry (DSC) shows that the thermal crosslinking for the methacryloyl groups starts at around 180 °C, making the system more suitable for use at higher processing temperatures. In general, poled polymeric NLO systems processed at higher temperatures, show better temporal stability at both normal ambient and elevated temperatures.

As in the case of the BPAZO/APAN system, in order to boost the NLO density, the methacryloyl functionalized azo dye DRMA (Disperse Red 19, functionalized with methacryloyl groups), was **synthesized** (the commercial dye is of insufficient purity to be used as the starting material for functionalization) and allowed to **crosslink** with the Polymer -11. The chemical structures of these materials are shown in Figs. 6 and 7.
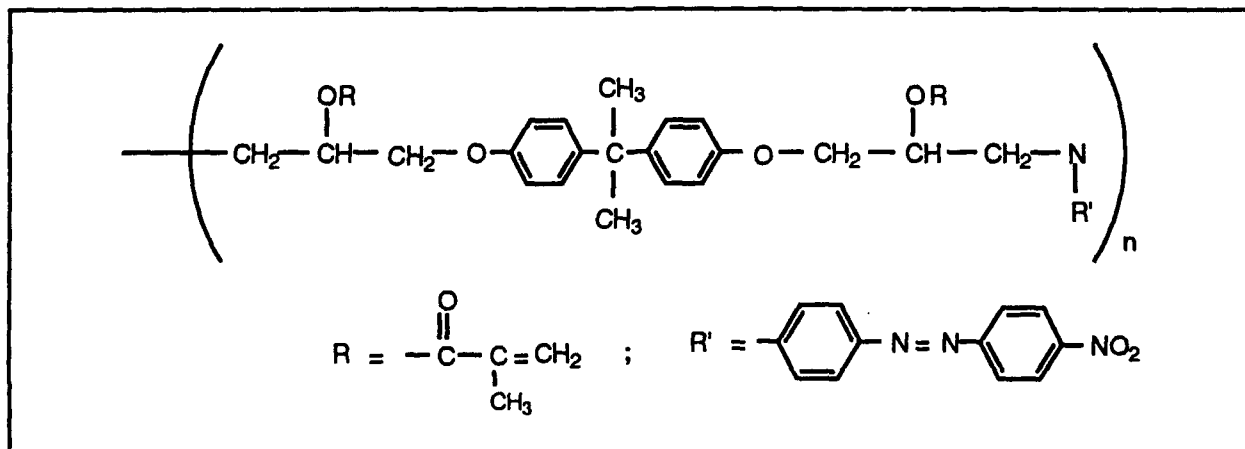

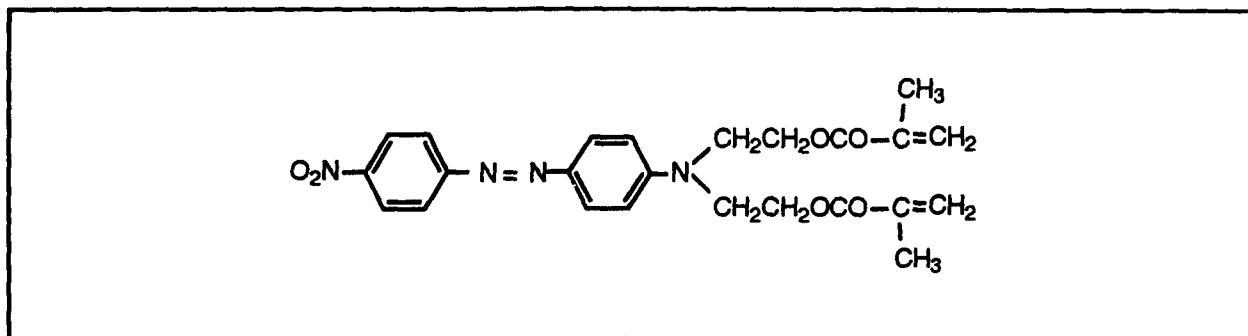Figure 6. The chemical structure of **Polymer-11**.

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Figure 7. The chemical structure of **DRMA**.

A large number of different compositions (1:0, 1:1, 1:2, 2:1 etc.) of Polymer-11/DRMA were processed at temperatures of 200 °C and 220 °C, and their spectroscopic and NLO properties were studied. Data for two of the best characterized compositions are shown in Table 4.

Table 4. Polymer 11/ DRMA Systems Prepared and Studied.

	Polymer 11	DRMA	Processing Conditions	d_{33} at 1.064 μm
Weight ratio	1	0	1h @ 200 °C	33.8
	1	1	1h @ 200 °C	28.0

Subsequently IPN systems of a number of different compositions (1:1, 2:1 etc.) of Phenoxysilicon (ASD/THPE) and Polymer 11/DRMA were prepared and characterized, some of which are shown in the following table (Table 5).

Table 5. IPN-B([ASD/THPE]/[Polymer 11- DRMA]) Systems Prepared and Studied.

	Phenoxysilicon (ASD/THPE)	Polymer 11-DRMA (2:1 w/w)	Processing Conditions	d_{33} at 1.064 μm
Weight ratio	1	1	1h @ 200 °C	32.0
	2	1	1h @ 200 °C	26.0
	1	1	0.5 h @ 220 °C	10.6
	2	1	0.5 h @ 220 °C	24.8

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Thin Film Sample Preparation and Characterization

Samples were spin-coated onto glass microscope slides in a Headway Research spin coater. They were simultaneously corona poled and cured at 200 °C for 1 hour or at 220 °C for 30 minutes. The NLO properties and their temporal stability of the resulting films were investigated by monitoring the decay of the second harmonic intensity with Nd:YAG (1.064 μm) radiation, as a function of time. Our preliminary studies indicate that most of these samples also exhibit the **extraordinary temporal stability at elevated temperatur** observed in the previous IPN-A system. The data for the retention of the NLO coefficient at 100 °C upto 169 hours is **extremely encouraging**, as shown in the graph in Fig. 8. At 169 hours, nominal d_{33} retentions of 96% (phenoxysilicon/[BPAZO/APAN]) and 93% (phenoxysilicon/ [Polymer 11/DRMA]) were observed.

We expect excellent long term stability, including resistance to short term high temperature excursions (**temperature spikes**), as may be encountered during device fabrication, integration with semiconductor devices and packaging, for these systems.
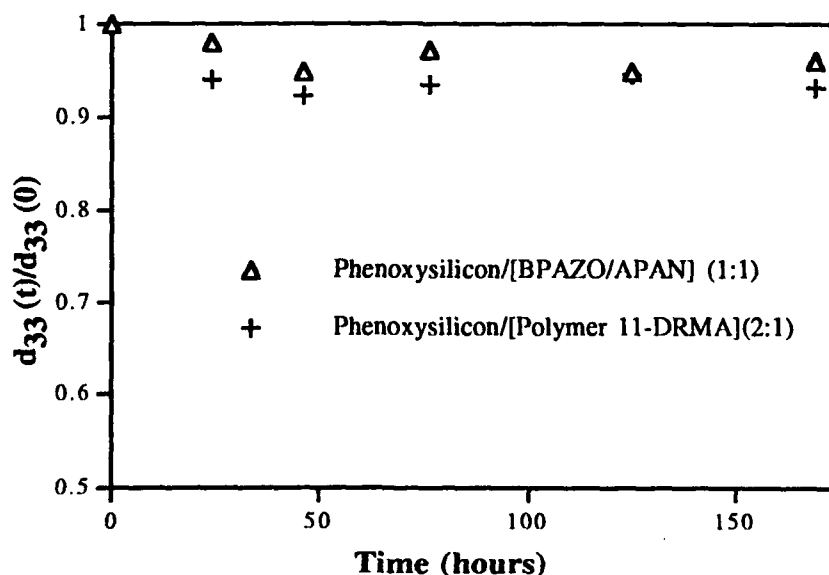

Figure 8. Temporal Stabilities of IPN-AB (Δ) and IPN-B (+) Systems at 100 °C.

The measured d_{33} values (to 32 pm/V at 1.064 μm) already equal or approach that observed for the previous system. *The measurement of the electro-optic (r_{33}) coefficients gave values of 18 pm/V at 633 nm and 6.5 pm/V at 1.3 μm.* Because of the higher NLO densities of the starting materials, significantly higher d_{33} and r_{33} values are obtainable, once the processing conditions are optimized. Additional improvements could be achieved with the use of more thermally stable NLO dyes.

Polymer 11 exhibits relatively **low optical loss** even at this early stage of development, where processing conditions have not been optimized. *Measurements on unclad slab waveguides gave values of 4.7 dB/cm at 830 nm and about 2dB/cm at 1.3 μm.*

IV. Conclusions

Rapid high temperature thermal processing was found to be of limited value in preventing chromophore loss in NLO siloxane systems during sol-gel processing. However NLO materials thus produced have fairly good temporal stabilities, even though the NLO coefficients are reduced by the loss of chromophores. IPN systems incorporating NLO siloxanes along with a second NLO polymer such as an NLO epoxy, appear to be *viable nonlinear optical materials for electro-optical device applications*. Their temporal stability is extraordinarily high, even at this early stage of development. The optical loss can be reduced by the proper choice of the polymer components. The electro-optic coefficients of the materials developed during the Phase I effort are moderate (upto 6.5 pm/V at 1.3 μm), but sufficient for the fabrication of usable devices. Materials with EO coefficients comparable to or better than that of lithium niobate, and low optical loss, can be expected to be produced, by a suitable choice of chromophores and optimization of processing conditions, in continuation of this work. The expected temporal stabilities should be sufficient for commercial and most military applications.

These enhancements will lead to the development of **high performance NLO materials** in the proposed follow on Phase II effort for the project.

Appendix A

We discuss here in fair detail the sample preparation procedures and techniques (with an emphasis on the chemical manipulation involved) and synthetic procedures used in carrying out the reported work. Additional details can be found in the literature referenced earlier and in this section. Physical techniques are described in Appendix B.

A.1 Sample Preparation Procedures

Polymer 11 thin film preparation

Mixtures of Polymer-11 and DRMA with weight ratios of 1/0, 2/1, 1/1, and 1/2 were dissolved in PGMEA (propylene glycol methyl ether acetate) (weight ratio of 2:10). The solutions were filtered through 0.2 μm membrane filters. The solutions were spin-coated on glass slides. Thin films were dried at 60 °C under vacuum. The films were poled and cured simultaneously at 220 °C for 1 h. The cured samples with heavy loading of dye (1/1 and 1/2) showed phase separation.

Preparation of IPNs

a. Phenoxysilicon/BPAZO (IPN-A)

To prepare thin film samples, a mixture of 0.4 g of ASD-DO3 and 0.3 g of THPE (molar ratio = 1.0:1.17) was dissolved in 6 g of a mixed solvent (propylene glycol methyl ether acetate : 1,4-dioxane = 3:1 (v/v)) containing 60 mg of water and 60 mg of N,N-dimethybenzylamine. The presence of water and base catalyst was to aid in the hydrolysis of the alkoxysilane. The solution was stirred for 4 h. In the mean time, a solution of 0.7 g of BPAZO in 2 g of the mixed solvent was prepared. After 4 h of stirring the first solution, the solution of BPAZO was added. The resulting solution contained a weight ratio of 1:1 BPAZO to ASD-DO3/THPE. The solution was filtered through 0.2 μm filters before it was spin-coated onto transparent microscope slides with a spinning rate of 1300 rpm to form optical quality thin films.

Corona poling with a wire-to-plane configuration was used. The corona field was applied as the temperature was raised to 80 °C. The temperature was then increased to the designated curing temperatures with the corona field on. The corona current was maintained at 2 μA with a potential of 4 kV while the poling temperature was kept at 200 °C for 60 min. The formation of the networks and the molecular alignment for the poled order proceeded simultaneously during this period. The sample was then cooled down slowly to room temperature before the corona field was discontinued.

b. Phenoxysilicon/[BPAZO / APAN] (IPN-AB)

A mixture of 0.1 g of ASD-DO3 [alkoxysilane dye derived from DO3, Fig. 3(a)] and 0.07 g of THPE (molar ratio = 1.0:1.17) was dissolved in 1 g of a mixed solvent (propylene glycol methyl ether acetate : 1,4-dioxane = 3:1 (v/v)) containing 20 mg of water and 20 mg of N,N-dimethybenzylamine. The presence of the water and base catalyst was to aid in the hydrolysis of the alkoxysilane. The solution was stirred for 4 h. In the mean time, a solution of 0.17 g of mixture of BPAZO and APAN with weight ratio of 2:1 in 2 g of the mixed solvent was prepared. After 4 h of stirring the first solution, both solutions were mixed together and the resulting solution contained a weight ratio of 1:1 ASD-DO3/THPE to BPAZO/APAN. Another solution was prepared in a similar manner with weight ratio of 2:1 ASD-DO3/THPE to BPAZO/APAN. The solutions were filtered through 0.2 μm filters before it was spin-coated onto transparent microscope slides with a spinning rate of 800 rpm to form optical quality thin films.

The samples were simultaneously poled and cured at 200 °C for 1 h.

c. Phenoxysilicon / Polymer 11 + DRMA (IPN-B)

The samples of this IPN system were prepared in a similar manner as described in Section b except that PGMEA, not the mixed solvent, was used. The weight ratios of Phenoxysilicon / Polymer 11 + DRMA were 1/1 and 2/1, while the weight ratio of Polymer 11:DRMA was 2:1.

The samples were simultaneously poled and cured at 220 °C for 30 min as well as at 200 °C for 1 h.

A2. Detailed Synthesis Procedures

We describe in detail, the synthetic procedures utilized to prepare the various chemical compounds, prepolymers and polymers used in the project. The synthesized materials were characterized by absorption spectra in the UV, visible, NIR and mid-IR regions, by DSC (differential scanning calorimetry). IR spectra were obtained on KBr pellets, or in the case of the polymers, on samples spin coated on KBr plates.

Synthesis of Alkoxysilane-derivatized Chromophores

The azo dyes, 4(4'-nitrophenylazo)-1-naphthol (chromophore 2) and 4(4'-nitrophenylazo)-resorcinol (chromophore 3) were obtained commercially (Aldrich Chemical Co.). The corresponding alkoxysilane derivatives were prepared by a phase transfer reaction with trimethoxysilyl-2-(p,m-chloromethyl)phenylethane (TMSCMPZ) [for silphenyl ASDs] or 3-chloropropyltrimethoxysilane in toluene/DMSO, using sodium hydroxide (NaOH) as the base, in the presence of tetrabutylammonium hydrogen sulfate (TBAH) as a catalyst [15]. Only the propyltrimethoxy derivatives, ASD2 and ASD3, described earlier, were used to prepare NLO siloxanes. It was found that the two-phase reaction medium was not necessary for these compounds. Hence, when a new batch of ASD2 was synthesized, the toluene/DMSO solvent system was replaced with neat DMSO. Also potassium carbonate (K_2CO_3) was used as the base, instead of sodium hydroxide (NaOH).

Synthesis of ASD-DO3

The NLO dye used in this system is an alkoxysilane dye derived from (3-glycidoxypropyl)trimethoxysilane (GPMS; from Hüls Petrarch Systems) and 4(4'-nitrophenylazo)aniline (Disperse Orange 3, or DO3, from Aldrich Chemical Co.). This ASD-DO3 was prepared by heating the mixture of GPMS and DO3 (molar ratio = 1.0:1.1) at 155

°C for 2 h under a nitrogen atmosphere. The unreacted DO3 was removed by vacuum sublimation at 140 °C for 1 h.

Synthesis of BPAZO

The synthesis of the thermally crosslinkable polymer (BPAZO) involved a two step reaction; the synthesis of the functionalized NLO prepolymer and the chemical attachment of the thermally crosslinkable group.

a. To prepare the functionalized NLO prepolymer, a mixture of 7.82 g of the diglycidyl ether of bisphenol A (DGEBA; obtained from Shell Chemical Co., Epon 828) and 5.81 g of DO3 (molar ratio = 1.0:1.1) was heated at 155 °C for 2 h under an inert atmosphere. This epoxy prepolymer, DGEBA-DO3, was washed by dispersing the prepolymer in an excess of toluene for several hours to remove the unreacted DO3 and the low molecular weight component. The washing was repeated 3-4 times.

b. To prepare the thermally crosslinkable polymer, BPAZO, a solution of 1.16 g (12.8 mmole) of acryloyl chloride (Aldrich Chemical Co.) in 50 mL of dry THF was slowly added dropwise to a solution of 7.98 g (13 mmole) of DGEBA-DO3 and 10.7 mL (76.9 mmole) of triethylamine in 200 mL of dry THF. The reaction was carried out in a dry-ice/2-propanol bath to keep the temperature around -78 °C. This reaction temperature was maintained for 4 h. The solution was stirred for an additional 16 h then the temperature was allowed to rise to room temperature. The resulted mixture was precipitated in 1800 mL of methanol. The dark orange product was filtered, washed with methanol, and dried under vacuum at room temperature.

Synthesis of Polymer-11

The prepolymer DGEBA-DO3, prepared in the manner just described in part a of the synthesis of BPAZO, was used as the starting material.

A solution of 8.2 g (78 mmole) of methacryloyl chloride (Aldrich Chemical Co., distilled) in 50 mL of dry THF was slowly added dropwise to a solution of 7.98 g (13 mmole) of

DGEBA-DO3 and 10.7 mL (76.9 mmole) of triethylamine in 200 mL of dry THF. The reaction was carried out in a dry-ice/2-propanol bath to keep the temperature around -78 °C. This reaction temperature was maintained for 4 h. The solution was stirred for an additional 16 h, then the temperature was allowed to rise to room temperature. The resultant mixture was precipitated in 1800 mL of methanol. The dark orange product was filtered, washed with methanol, and dried under vacuum at room temperature.

Synthesis of DRMA

A solution of 1.9 g (18 mmole) of methacryloyl chloride (Aldrich Chemical Co., distilled) in 25 mL of dry THF was slowly added dropwise to a solution of 2.0 g (6 mmole) of disperse red 19 and 2.5 mL (18 mmole) of triethylamine in 95 mL of dry THF. The reaction was carried out in a dry-ice/2-propanol bath to keep the temperature around -78 °C. This reaction temperature was maintained for 4 h. The solution was stirred for an additional 16 h, then the temperature was allowed to rise to room temperature. The resulted mixture was precipitated in 1800 mL of water. The orange dye was filtered, washed with water. The crude product was then recrystallized in hexane. The bright orange dye was dried under vacuum at room temperature.

Synthesis of APAN

A solution of 0.5 g (6 mmole) of acryloyl chloride (Aldrich Chemical Co.,) in 25 mL of dry THF was slowly added dropwise to a solution of 2.0 g (6 mmole) of 4-(4-nitrophenylazo)resorcinol and 2.5 mL (18 mmole) of triethylamine in 95 mL of dry THF. The reaction was carried out in a dry-ice/2-propanol bath to keep the temperature around -78 °C. This reaction temperature was maintained for 4 h. The solution was stirred for an additional 16 h, then the temperature was allowed to rise to room temperature. The resultant mixture was precipitated in 1800 mL of water. The bright orange dye was filtered, washed with water, and dried under vacuum at room temperature.

Appendix B

We now discuss physical sample fabrication techniques followed by the methods used for the optical characterization of the materials studied.

B.1 Sample Fabrication Techniques

Spin Coating

Spin coating is a well established technique for depositing uniform thin films of materials from solution onto rigid substrates, and is utilized extensively in the electronics and semiconductor industry for coating photoresists, planarizing coatings, passivation coatings and similar materials on silicon, glass, quartz and ceramic substrates [16]. It is currently used widely in the NLO polymer research community to deposit uniform polymer coatings for characterization and device fabrication. The thickness of the coating can be adjusted from submicron levels to tens of microns, by adjusting the viscosity of the coating solution, the spin rate and the spin time. Sample solutions were applied from an automatic pipet onto glass microscope slides held in the vacuum chuck of a Headway Research spin coater, which allowed spin speeds and spin times to be preset. The resulting films were dried and processed as described in section A.1 earlier.

Corona Poling

Corona poling is extensively used to orient second order NLO polymers, since high orientation fields can be obtained [17], and deposition of electrodes are not required. The procedure was carried out in a laboratory scale apparatus, shown schematically in Figure 9. A wire-to-plane configuration is used, with the 100 μm (4 mil) diameter tungsten corona wire positioned 1 cm away from the sample surface. The apparatus is equipped with an aluminum hot stage for the samples, which could be heated electrically by a ceramic-insulated heating element, or cooled by circulating water through cooling passages in the stage. The sample temperature could be controlled to >300 °C, by adjusting the heater power with a Powerstat™ (variable autotransformer). The d.c. voltage applied to the corona wire could be

varied from 0-20 kV, by changing the input line voltage to the high voltage power supply with another Powerstat.™ The sample temperature was monitored by a type J thermocouple in conjunction with a Tegam digital thermometer, and the total poling current was measured with a Keithley model 169 digital multimeter.
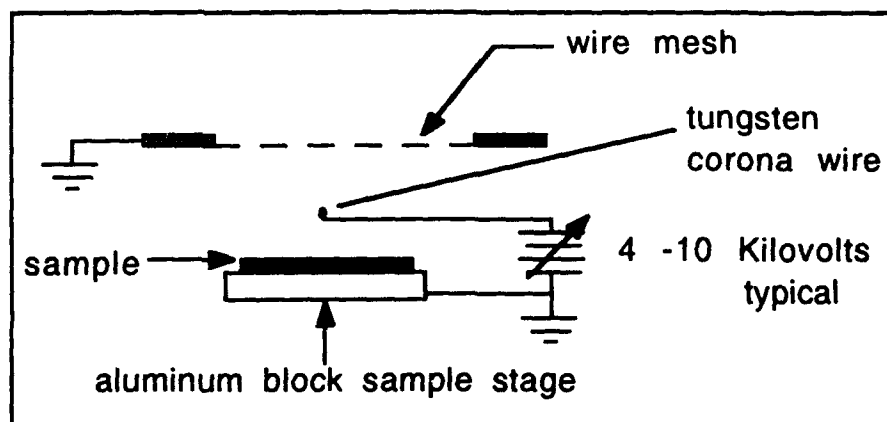

Figure 9. Corona Poling Apparatus used in Orienting NLO Polymers

An effective poled area, of approximately 1.5 cm x 2.5 cm could be easily obtained in our apparatus. Larger areas can be poled by using a multiwire corona poling apparatus.

B.2 Measurement of Linear and Nonlinear Optical Properties: Techniques

We describe here some of the apparatus and techniques used to characterize the optical properties of the polymers, chromophores and other materials developed during our research and development activity.

Linear Optical Properties

While the main thrust of the research proposed here is development of optimized NLO materials, the importance of linear optical measurements cannot be overemphasized. Linear optical properties of materials are important not only because they help characterize these materials, but are also extremely important parameters for any optical device design and fabrication. Sometimes even if a material has extremely large NLO coefficients, it is not usable because of excessive loss either due to scattering or absorption. The refractive

indices are important parameters for the design of waveguides and active devices such as EO modulators.

The refractive indices of the materials were measured by ellipsometry using a Rudolph Research ellipsometer and by wave guiding techniques. Both of these methods yield accurate measurements of refractive index and film thickness and their use for such purposes is well established. Waveguiding has the added advantage of estimating absorption and scattering losses in the material on a substrate which may be used for device fabrication. Linear absorption measurements were made on a Perkin Elmer Lamda-9 dual beam UV-Vis-NIR spectrophotometer which can cover a wavelength range of 190-3300 nm.

The optical loss of polymer slabwaveguides were determined at 1.3 μm, as well as at other wavelengths, including 830 nm. This measurement is based on the assumption $I = I_0 \exp(-\alpha x)$ where I is the intensity scattered from the waveguide at any point, x is the position along the waveguide streak, I_0 is the intensity at $x = 0$, and α is the attenuation coefficient. The experimental set-up for slab waveguide loss measurement is shown in Figure 10, in which a prism is used for coupling.
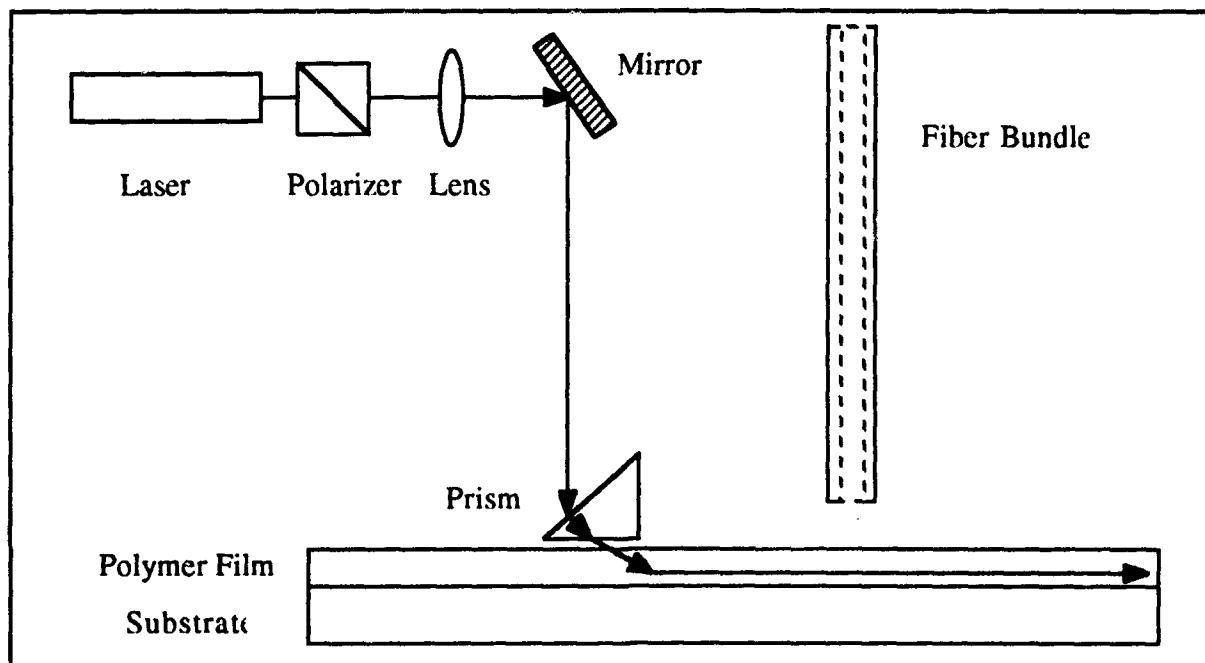

Figure 10. The experimental set-up for slab waveguide optical loss measurement.

An optical fiber bundle is utilized as the probe to collect light scattered from the waveguide and couple it to the photodetector head of a Newport model 835 optical power meter. The fiber bundle is held with a fiber positioner which is mounted on a translation stage. This fiber probe can be adjusted and scanned along the length of the bright streak formed by the guided beam. An **IR video camera** is utilized to monitor the waveguide coupling and could be interfaced with a personal computer to measure the scattered light from the waveguide along the bright streak. The waveguide loss is determined by the slope of a plot of $\log_{10}(I)$ v.s. x. At 1.3 μm, a Hamamatsu model C1000 type O3 video camera was used both to monitor the coupling and to estimate the optical loss. The absorption loss of polymeric materials at 1.3 μm is smaller than at shorter wavelengths so that a significant part of the waveguide loss is due to scattering in the polymer film and from the rough film surfaces. The waveguide loss can be minimized by the adequate purification of the polymer and appropriate choice of the cladding layer.

Second-Order NLO Properties

Second-order NLO properties of the polymeric materials were measured by the second harmonic generation (SHG) technique. A Quantel model 660A, Q-switched Nd:YAG laser (λ = 1.064 μm) with a pulse width of 20 ns and a pulse energy of 45 mJ was used as the fundamental source. A Y-cut quartz crystal (d_{11} = 0.50 pm/V) was used as the reference material for the calibration of the frequency-doubled signal from the sample to evaluate the second harmonic coefficient d_{33} of the polymeric NLO material. The setup shown in Fig. 11, was used. The thin film polymer sample was set perpendicular to the incoming p-polarized fundamental beam. The sample was then rotated with relation to the fundamental beam, and the second harmonic (SH) signal generated in the process was monitored by the photomultiplier connected to a Stanford Research Systems (Sunnyvale, California) model SR250 boxcar integrator, so that the signal could be read and averaged. The trigger signal for the boxcar was obtained from a high speed photodiode, which sampled a small portion of the laser beam through a beam splitter. A neutral density filter was positioned before the trigger

photodiode, to protect it from damage from the high peak laser power. An identical second measurement channel was used to monitor the SH signal from the quartz reference, and was triggered from the same photodiode.
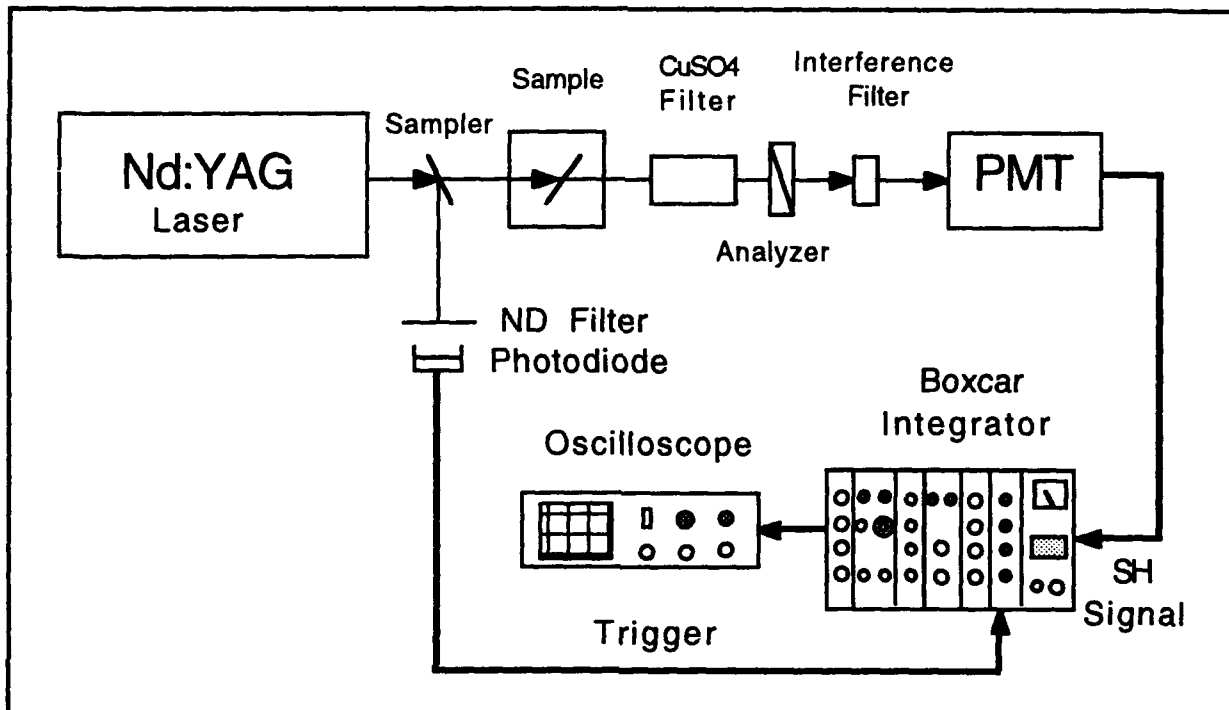

Figure 11. Schematic of the SHG Experiment to Determine d Coefficients.

The transmitted fundamental beam was blocked by aqueous $CuSO_4$ solution in a cuvette, while a narrow band interference filter centered at 532 nm allowed the second harmonic beam to pass. The second-order nonlinear optical coefficient, d, of the poled polymer was obtained using the Jerphagnon and Kurtz [18] formula for SHG intensity, $I(2\omega)$, as follows:

$$I(2\omega) = \frac{(512\pi/A)t_\omega^4 T_{2\omega} d^2 t_0^2 p^2 I^2(\omega)\sin^2\psi(\theta)}{(n_\omega^2 - n_{2\omega}^2)}$$

where $I(\omega)$ is the fundamental power, A is the beam area, θ is the incident angle, t_0, t_ω and $T_{2\omega}$ are the transmission factors, p is a projection factor, and n_ω and $n_{2\omega}$ are refractive indices of the polymer for the fundamental and the SH, respectively and $\Psi(\theta)$ is an angular factor related to the sample thickness, the wavelength of the fundamental wave, and the

refraction angles. By measuring the SH intensities as a function of the fundamental and second harmonic polarizations, the d values can be readily determined. Calculations were carried out using in-house computer programs.

The fundamental laser frequency was shifted to a longer wavelength, 1.542 μm by stimulated Raman scattering of the 1.064 μm laser radiation in a high pressure methane cell. For temporal stability measurements at elevated temperatures, the sample was stored in an oven at the chosen temperature, briefly removed for measurement and then returned to the oven until the next measurement.

Electro-optic Coefficient Measurements

The electro-optic r coefficients presented in this report were measured by a reflection technique developed by Teng and Man [12]. A more detailed theoretical analysis of the method has been given by Schildkraut [19].

The polymer sample was spin-coated onto a glass microscope slide carrying a transparent conducting indium tin oxide (ITO) coating (vendor: Thin Film Devices, Anaheim, California), which serves as one of the electrodes for EO modulation. A 500-600 Å layer of gold was evaporated on top of the polymer film, through a shadow mask, to serve as a reflecting second electrode. A laser beam was made incident on the back of the glass substrate, with its polarization set at 45° to the plane of incidence, so that the perpendicular (s wave) and parallel (p wave) components are equal in magnitude. The method utilizes the change in phase retardation between the s and p waves in the reflected beam, with electric field modulation, to determine the EO coefficient. Thus it is related to the birefringent phase retardation methods [20] used for crystalline samples. A correction can be applied for the static birefringence due to poling [19]. It can be shown that approximately :

$$r_{33} = 3 \ \lambda I_m \ (n^2 - \sin^2\theta)^{3/2} \ (n^2 - 2\sin^2\theta)^{-1} \ (1/4\pi V_m I_c n^2)(1/\sin^2\theta)$$

where n is the refractive index, V_m is the modulation voltage, I_c is the half intensity, θ is the angle of incidence and I_m is the amplitude of the optical intensity modulation. Thus r_{33}, the EO coefficient perpendicular to the direction of optical propagation in the film, can be readily determined, without having to recourse to waveguiding techniques. The measurement apparatus is shown in Fig. 12.
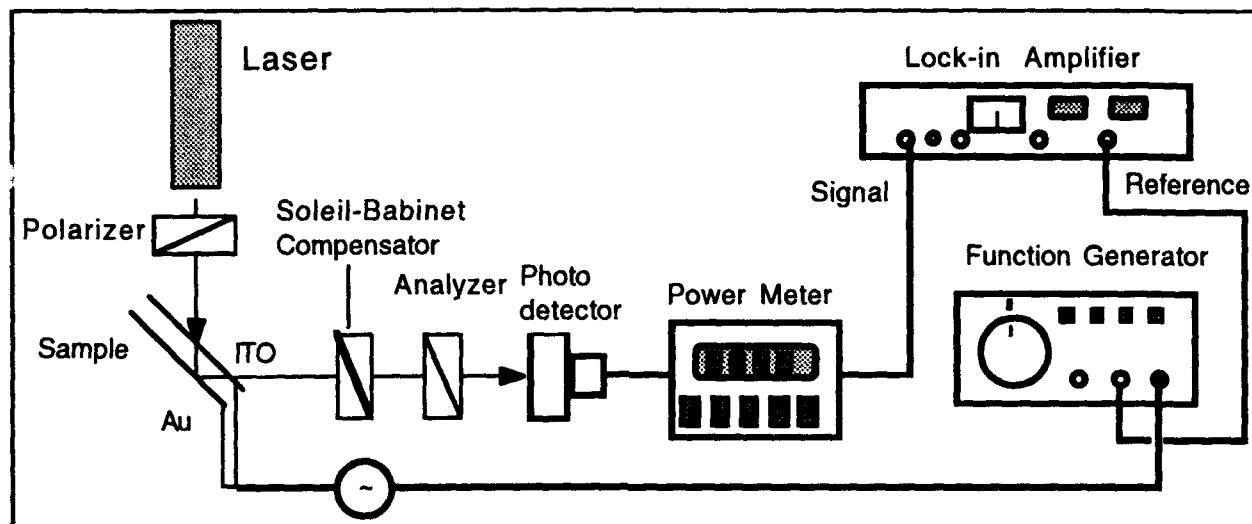

Figure 12. Apparatus for EO Coefficient Measurement by the Reflection Technique [12].

Sinewave modulation at ~2 kHz, with an amplitude of several volts, was applied from a Hewlett Packard model 3311A function generator, while a large area PIN photodiode (Newport model 818-SL) coupled to a Newport 815 power meter, followed by a Stanford Research Model SR510 lock-in amplifier served as the detector. The polarizers and the Soleil-Babinet compensator were from Optics for Research. The light source was a 5 mW HeNe laser for measurements at 633 nm, and a Lasermax, 5.8 mW diode laser was used for measurements at 1.3 μm.

The data was analyzed in accordance with reference [12], which also gives additional details on the measurement procedure. As expected the EO coefficients at 1.3 μm are significantly smaller than those at 633 nm. However, the values obtained, as presented earlier, such as the 6.5 pm/V at 1.3 μm for the IPN-B system, are still sufficient for many

electrooptical devices. The Phase II effort is expected to yield materials with significantly higher *r* coefficients and low optical loss.

EFISH Measurements

EFISH measurements have been found to be extremely useful in evaluating the potential nonlinear optical properties of NLO chromophores [21,22,23]. A new EFISH measurement cell of improved design, based on [24] was constructed, and is shown in Fig. 13. This has the advantage that there is no SH wave from the glass windows, and the construction is actually simpler. A 1mm cell spacer is used, so the cell, when driven by a Velonex Model 350 High Power Pulse Generator (0-20kV output, not 0-2kV as misstated in the progress report [8]), provided measurements to electric fields as high as 200kV/cm. In the Phase I work we used only a series of structurally similar azo dyes, so that the trend in the $\mu\beta$ product could be predicted without measurement. However this measurement setup is going to be more useful in the Phase 2 work, where different types of chromophores are going to be utilized.
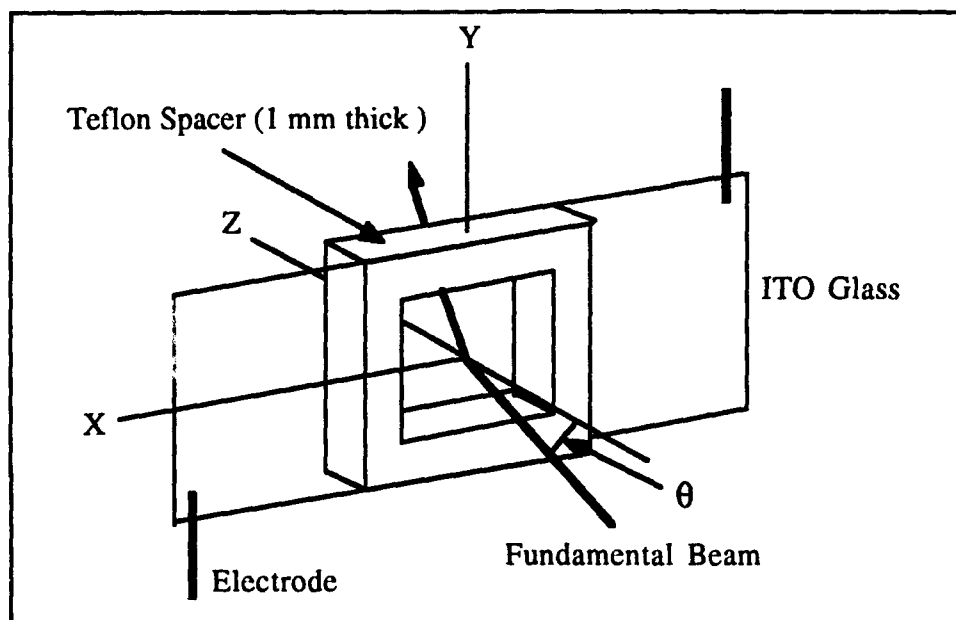

Figure 13. Sample Cell for EFISH Measurements.

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